Researchers propose post-synthetic modification of covalent organic frameworks for carbon dioxide electroreduction

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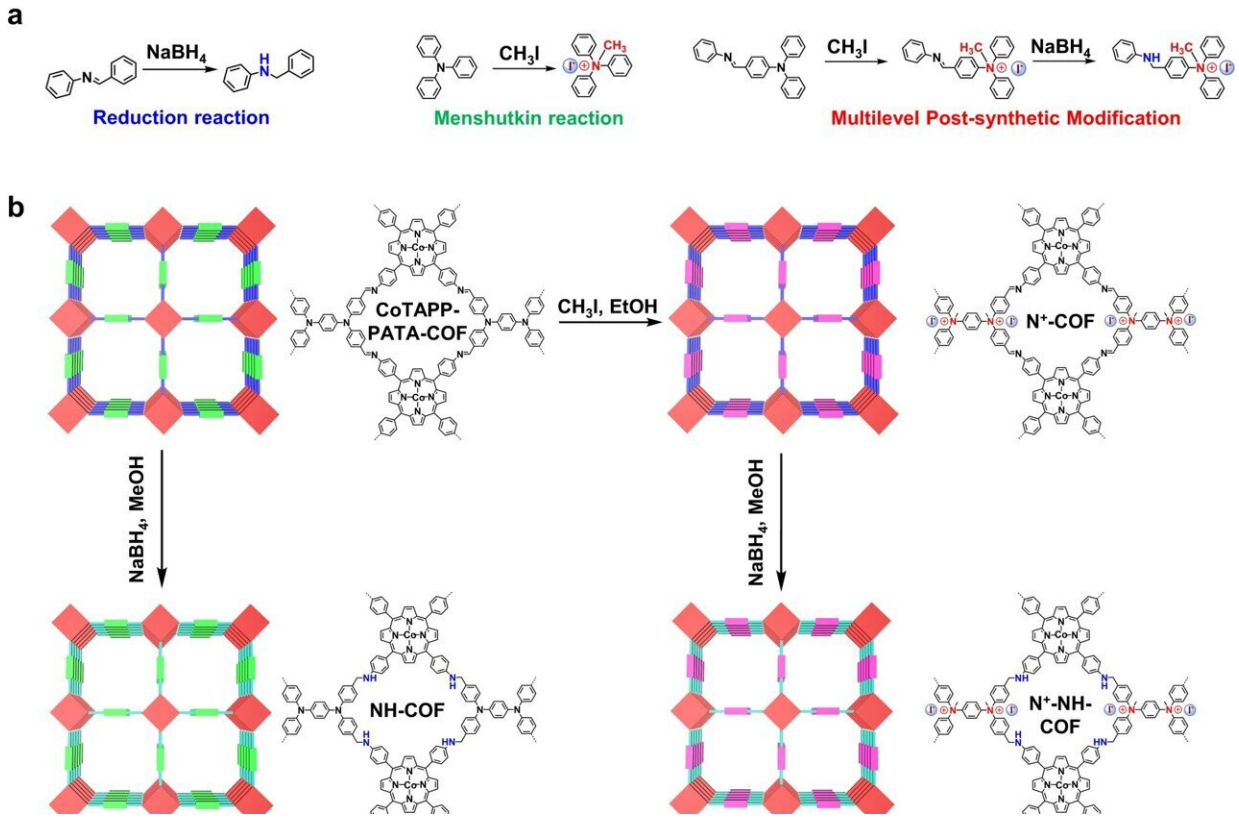

Schematic illustration of multilevel post-synthetic modification. **a** Effects of reduction reaction, Menshutkin reaction and multilevel post-synthetic modification on the bond change and charge state. **b** The synthesis of N^+-COF, NH-COF and N^+-NH-COF from the base COF (CoTAPP-PATA-COF). Credit: *Nature Communications* (2023). DOI: 10.1038/s41467-023-39544-9

Covalent organic frameworks (COFs), possessing ordered pores and high-precision functionalization, are regarded as an ideal class of templates to construct catalysts for electrocatalytic carbon dioxide reduction reaction (CO_2RR).

C-N bonds can improve adsorption of CO_2 and ionic skeletons can promote charge transfer, further enhancing conductivity. However, direct bottom-up synthesis can hardly realize co-existence of C-N bonds and ionic frameworks due to the electrostatic repulsion and weak strength of the linkage.

A research team led by Prof. Zeng Gaofeng and Assoc. Prof. Xu Qing from the Shanghai Advanced Research Institute (SARI) of the Chinese Academy of Sciences has proposed a multilevel post-synthetic modification strategy to construct catalytic COFs towards CO_2RR with high activity and selectivity.

The results were published in *Nature Communications*.

Catalytic COFs synthesized by the post modification showed a maximum turnover frequency value of 9922.68 h^{-1} at –1.0 V and the highest faradaic efficiency of 97.32% at –0.8 V, which were higher than that of the base COF and the single-modified COFs.

Electrocatalysis tests and characterizations revealed that C-N bonds could improve catalytic selectivity and ionic skeleton contributed to higher activity.

Furthermore, theoretical calculations illustrated that the easier formation of immediate *CO from COOH* was the rate-determined step, and methyl groups strengthened electron density.

This work provides a deeper understanding of COFs in CO_2 reduction

reaction. It sheds light on constructing multilevel post-synthetic modification COFs towards tailored activity and high stability.

More information: Minghao Liu et al, Post-synthetic modification of covalent organic frameworks for CO_2 electroreduction, *Nature Communications* (2023). DOI: 10.1038/s41467-023-39544-9

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